

# Optical power limiting with photoinduced anisotropy of azobenzene films

Pengfei Wu, Reji Philip, Ramesh B. Laghumavarapu, Janakriam Devulapalli, Devulapalli V. G. L. N. Rao, Brian R. Kimball, Masato Nakashima, and Barry S. DeCristofano

We study the power-limiting properties of photoanisotropic azobenzene films with low-power lasers. The *trans-cis* photoisomerization and molecular reorientation of azobenzene molecules induced by polarized laser beams result in intensity-dependent anisotropic effects. Consequently, the transmittance of the input beam that passes through the film between two crossed polarizers becomes enhanced at low intensities and clamped at high intensities. The limiting threshold is adjustable by changing the intensity of excitation beam. © 2003 Optical Society of America

OCIS codes: 190.4360, 230.4320, 260.1440, 310.6860.

## 1. Introduction

The rapid development of laser technology has made portable laser systems with high power and energy available. The lasers are widely used for many applications and have greatly advanced scientific research. As they are used everywhere, the odds of a laser beam accidentally hitting a person are increasing. Even low-power lasers can damage human eyes or photosensors. As such, studies of optical power limiting are receiving a lot of interest. Several optical techniques with various materials including inorganic, organic, and biological molecules have been used for such applications. Nonlinear absorption effects including excited-state absorption,<sup>1</sup> reverse saturable absorption,<sup>2</sup> and multiphoton absorption<sup>3–5</sup> are widely investigated with high-power pulsed lasers in both theory and experiment. Light scattering is also used to limit the optical power when a strong beam is incident on some materials,<sup>6,7</sup> and it can enhance the nonlinear absorption. Another important nonlinear optical effect used for the power

limiting is beam diffusing, which originates from the change of spatial distribution of the refractive index and manifests as self-defocusing,<sup>8</sup> beam fanning (diffusive photovoltaic thermal effects),<sup>9</sup> and the Kerr effect.<sup>10</sup> The filtering features associated with the holographic technique<sup>11,12</sup> and photonic bandgap materials<sup>13,14</sup> are also useful for power-limiting applications. Recently, polarization rotation in resonant Faraday media sandwiched between crossed polarizers<sup>15</sup> and in bacteriorhodopsin materials placed between a pair of parallel polarizers<sup>16</sup> has been studied theoretically and experimentally and could be used for optical limiting applications. These polarization rotation techniques may offer many advantages, such as low-fluence threshold, high-intensity range, and ease of improvement with new materials for practical applications, particularly for protecting human eyes and sensitive optical sensors that can be damaged by even low-power laser beams. In this paper we present a study on photoinduced anisotropic effects of azobenzene polymer films and its application to power limiting. The experimental results we obtained with the crossed polarizer arrangement illustrate clamping close to that of an ideal optical limiter.

## 2. Experiments

### A. Sample Film Preparation and Optical Characteristics

An azobenzene material of 4-dimethylaminoazobenzene is used in our studies. The material possesses optical properties of both *trans-cis* photoisomerization and photoinduced reorientation. The azobenzene molecules are embedded in the poly-

P. Wu, R. Philip, R. B. Laghumavarapu, J. Devulapalli, D. V. G. L. N. Rao (raod@umb.edu) are with the Department of Physics, University of Massachusetts, Boston, Massachusetts 02125. R. Philip's permanent address is Raman Research Institute, Bangalore 560 080, India. B. R. Kimball, M. Nakashima, and B. S. DeCristofano are with the Material Science Team, U.S. Army Soldier Systems Center, Natick, Massachusetts 01760.

Received 17 December 2002; revised manuscript received 16 April 2003.

0003-6935/03/224560-06\$15.00/0

© 2003 Optical Society of America

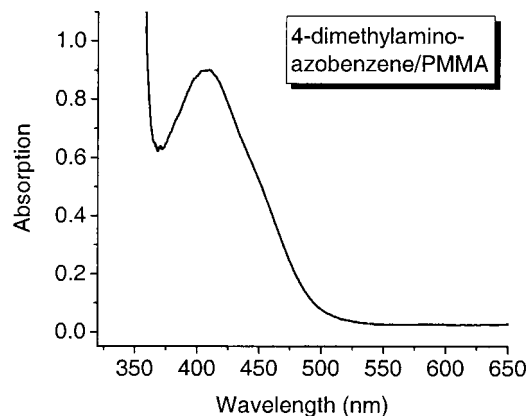


Fig. 1. Absorption spectrum of 4-dimethylamino-azobenzene PMMA film.

mer matrix of polymethylmethacrylate (PMMA). To prepare the sample, initially azobenzene and PMMA are dissolved separately in chloroform at approximately 60 °C. The solutions are then uniformly mixed by stirring them together for an hour and are then coated onto an optical-quality glass substrate. The thickness of the azobenzene polymer film is approximately 50  $\mu\text{m}$ , and the concentration of the azobenzene molecules in polymer is 5% by weight. The film normally transmits 25% of the incident light at 532 nm. Figure 1 shows the absorption spectrum of 4-dimethylamino-azobenzene PMMA film. It has a broad absorption band with a maximum absorption at 408 nm (full width at half-maximum is approximately 100 nm) because of the  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  transitions of the azobenzene molecules. The films also absorb light intensively in the UV region around 350 nm, which originates from the absorption of the PMMA polymer. Because of the overlap of absorption of its two isomers (*trans* and *cis*), the light-induced absorption change is small.<sup>17</sup>

Materials exhibiting photoinduced anisotropy have potential applications in information storage and information processing.<sup>18–20</sup> It is well known that photoinduced molecular reorientation generally takes place in fluid systems such as liquid crystals. Nevertheless, by the application of polarized light it is possible to reorient a random distribution of azobenzene molecules in solid matrices through a photoinduced *trans-cis-trans* isomerization process.<sup>21,22</sup> Our samples of PMMA polymer film doped with 4-dimethylamino-azobenzene present large photoinduced anisotropy. The molecule of 4-dimethylamino-azobenzene undergoes an isomerization process with excitation of light in the absorption band, shown in Fig. 2.

In the absence of light the azobenzene exists in the *trans* form that is stable with an elongated structure, whereas the photoinduced *cis* molecules have a bent shape and can revert to the *trans* form by thermal or photo-assisted isomerization with another wavelength. The length of the azobenzene segment in

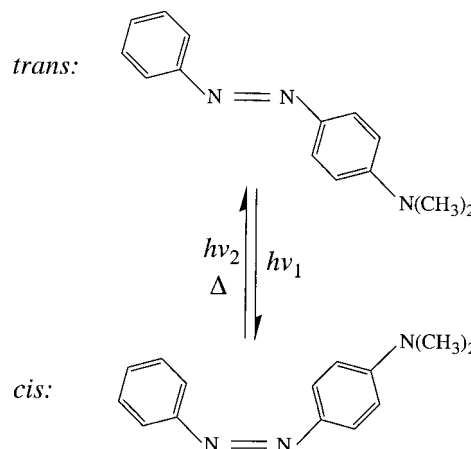


Fig. 2. Isomerization process of 4-dimethylamino-azobenzene.

the *trans* form is approximately 1.0 nm whereas that of the *cis* is approximately only 0.56 nm. This change of molecular dimension results in the bent *cis* form rotating more easily than the *trans*. When the transition dipole moment of a molecule becomes perpendicular to the polarization of the exciting light, its interaction with the light field ceases. Thus, after sufficient irradiation of an ensemble of azobenzene chromophores, an enhancement of transition moments perpendicular to the polarization vector of the excitation light is achieved. It is this local ordering that leads to photoinduced anisotropy in the medium.

## B. Experimental Arrangement

Figure 3 displays the experimental arrangement for studies of photoinduced anisotropy and optical power-limiting application. A 532-nm output from a frequency-doubled cw Nd:YAG laser is polarized by polarizer  $P_1$  and divided into a reflected beam (exciting beam) and transmitted beam (input beam) by a beam splitter. The exciting beam is directed through a variable attenuator and polarization rotator to the thin-film sample. The input beam travels through a variable attenuator and aperture toward the film and then to a laser powermeter through a second polarizer  $P_2$ . The polarizers  $P_1$  and  $P_2$  are crossed. The polarization of the exciting beam is fixed at an angle of 45 deg to that of the input beam. Both beams overlap spatially on the sample, and the

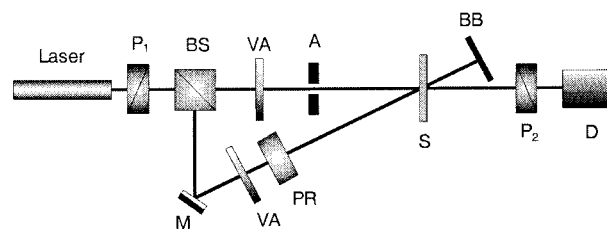


Fig. 3. Experimental setup.  $P_1$ ,  $P_2$ , polarizers; BS, beam splitter; VA, variable attenuator; PR, polarization rotator; A, aperture; S, sample film; BB, beam block; D, detector.

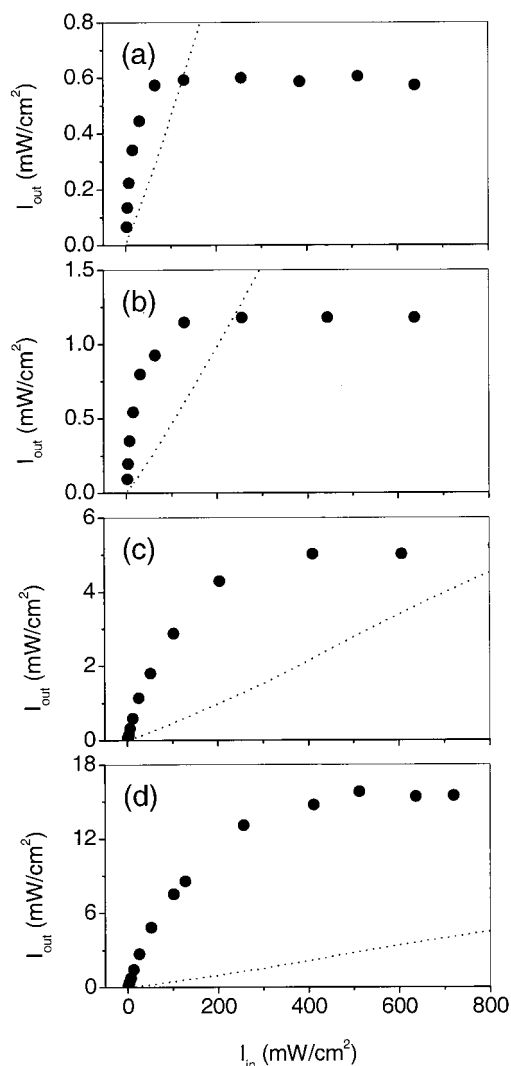


Fig. 4. Optical power limiting based on photoinduced anisotropy of the azobenzene film.  $I_{in}$  and  $I_{out}$  are the intensities of the input beam before polarizer  $P_1$  and behind polarizer  $P_2$ , respectively. The intensity values for the exciting beam are (a) 8.0, (b) 15.9, (c) 42.4, (d) 91.6 mW/cm<sup>2</sup>. The dotted curves are the results without the exciting beam.

aperture ensures that the diameter of the input beam is less than that of the exciting beam.

### C. Experimental Results and Discussion

With an intensity increase of the input beam, we obtain the power-limiting property by using the azobenzene film. Figure 4 shows the experimental results. The dotted curves represent linear transmission of the input beam in the absence of the exciting beam. In the presence of the exciting beam, we found that the transmission of the input beam becomes nonlinear. With the increase of the input intensity, the results show a nearly perfect power-limiting feature. In addition, we also found that it is possible to change the clamping threshold by choosing a different exciting intensity. For low intensities of the input beam, the presence of the exciting beam

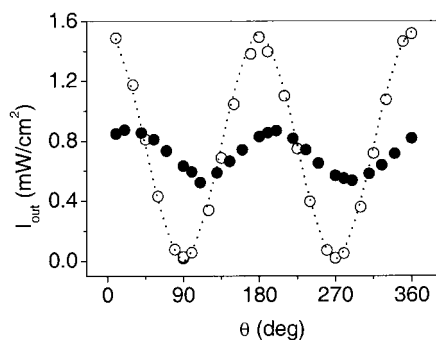


Fig. 5. Photoinduced anisotropy in the azobenzene film. The input intensity is 6.4 mW/cm<sup>2</sup>. Open circles depict the output of the input beam in the absence of the exciting beam, and the dotted curve is a  $\cos^2 \theta$  function. Solid circles show the output of the input beam in the presence of the exciting beam of intensity 91.6 mW/cm<sup>2</sup>.

significantly enhances the output. At an intensity of 6.4 mW/cm<sup>2</sup> of the input beam, the measured transmission is 0.45% without the exciting beam, whereas it rises to 3% with an exciting intensity of 8 mW/cm<sup>2</sup> and to 11.6% with an exciting intensity of 91.6 mW/cm<sup>2</sup>. Thus the linear transmission of the input beam can be enhanced by the exciting beam in this regime. On the other hand, for high intensities of the input beam, this enhanced output becomes limited and is finally clamped. For example, at the exciting intensity of 8 mW/cm<sup>2</sup>, an increased intensity of 639 mW/cm<sup>2</sup> of the input beam results in a drastic drop of the transmission to 0.09%. Therefore, with our experimental arrangement, it is not only feasible to achieve the power-limiting feature but also easy to change the clamping threshold by choosing a different exciting intensity.

The mechanism of power-limiting properties can be understood with the photoinduced anisotropy of the azobenzene film. The photoinduced anisotropy including both photoinduced birefringence and photoinduced dichroism are intensity dependent in azobenzene film, which results in the possibility of controlling the output intensity with the input intensity. To investigate the photoanisotropy, we first measured the transmission of the input beam for different angular orientations  $\theta$  of the analyzer  $P_2$  ( $\theta = 0$  being parallel to the polarization direction of polarizer  $P_1$ ). The results are shown in Fig. 5. In the absence of the exciting beam, the angular intensity distribution of the transmitted input beam fits closely to a  $\cos^2 \theta$  function, whereas in the presence of the exciting beam the output is transformed to elliptical polarization. This happens because of the photoanisotropic effect of the azobenzene film induced by the linearly polarized exciting beam. The transition moment of the azobenzene molecule lies along the molecular axis, and only these molecules with their axis orientation parallel to the electric vector absorb light and are then isomerized from *trans* form to *cis* form. The *cis* form is unstable and will go back to *trans* form where it may be isomerized to *cis* form

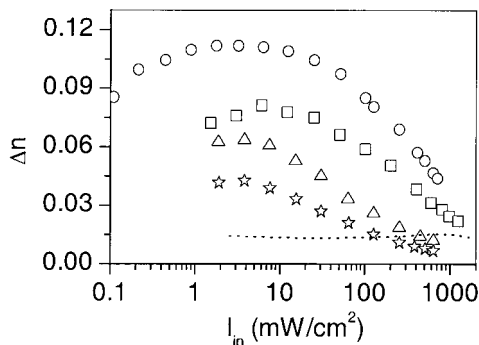


Fig. 6. Variation of  $\Delta n$  with the intensity of the input beam. The intensities of the exciting beam are the following: dotted curve, nil; circles, 91.6 mW/cm<sup>2</sup>; squares, 42.4 mW/cm<sup>2</sup>; triangles, 15.9 mW/cm<sup>2</sup>; stars, 8.0 mW/cm<sup>2</sup>.

again if its transition moment is not perpendicular to the electrical direction of the light field. The repeated *trans-cis-trans* isomerization results in the alignment of azobenzene molecules in the direction perpendicular to the polarization of the exciting beam. This molecular alignment causes the photoinduced birefringence that makes the output polarization elliptical and the photoinduced dichroism that makes the semimajor axis of the ellipse shift through a rotation angle from the  $\theta = 0$  plane. Both mechanisms contribute to the optical power-limiting property. However, for the azobenzene film, the photoinduced birefringence will be dominated as compared with the photoinduced dichroism. The semiminor axes of the ellipse depend on the relative values of the input and exciting intensities. The photoinduced polarization ellipse originates from a phase retardation  $\Gamma$ , which is given by  $\Gamma = \Delta n \pi d / \lambda$ , where  $d$  is the film thickness and  $\lambda$  is the input wavelength.  $\Delta n = n_{\perp} - n_{\parallel}$  is the birefringence where  $n_{\perp}$  and  $n_{\parallel}$  are the respective components of the index of refraction perpendicular and parallel to the exciting beam polarization. Estimates of the phase retardation  $\Gamma$  can be obtained from the transmission equation  $I = I_0 \sin^2 \Gamma$ , where  $I_0$  is the input intensity before  $P_2$  and  $I$  is the intensity after  $P_2$ . Figure 6 shows the results of birefringence  $\Delta n$  as a function of input intensity. When the exciting beam is absent,  $\Delta n$  is close to zero. In the presence of the exciting beam,  $\Delta n$  is higher and shows an initial increase with input intensity, which is followed by a decrease toward zero at higher input intensities. From a device point of view, this characteristic is more desirable because it ensures enhanced transmission at low intensities and limiting at high intensities. The observed limiting can be explained on the basis of the results of intensity-dependent photoinduced anisotropy of the azobenzene film. In the region of weak intensity of the input beam, the photoinduced anisotropy is relatively large and changes the polarization of the input beam that leads to an enhanced transmission through the crossed polarizers. On the other hand, with a relatively strong intensity of the input beam, the photoanisotropic effect is reduced, so

the input beam becomes blocked by the crossed  $P_2$ . In addition, the photoinduced anisotropy also depends on the intensity of the exciting beam. With higher exciting intensity, the photoinduced birefringence of azobenzene film is shifted to the region of larger values. Therefore, by choosing the values of exciting intensity we can easily control the clamping threshold of power limiting.

The optical processes such as nonlinear absorption, nonlinear scattering, and beam diffusing have been extensively investigated for power limiting with various materials,<sup>1-10</sup> and there is recent interest in nanoscopic materials as well.<sup>23-25</sup> However, none of them provide smooth and complete clamping of the output as observed in the present case. In addition, we note that use of crossed polarizers in our scheme results in a novel normally opaque (NO) optical limiter, in the sense that it is essentially an opaque device in which a transparency at low inputs is induced by photoinduced anisotropy. Conventional optical limiters are normally transparent (NT) designs in comparison, in which an opacity at high inputs is induced by nonlinear optical phenomena. In general, a NO design offers an unmistakable advantage in terms of detector safety. To appreciate this point, in the present case let us imagine two worst-case situations where either the exciting beam becomes accidentally blocked or the film becomes transparent by photodamage. In both cases the output will remain within safe limits by virtue of the crossed polarizers. On the other hand an NT design with parallel polarizers can severely imperil detector safety under such circumstances (we repeated the experiments with parallel polarizers, but the nonlinear transmission that we obtained was not as spectacular).

The transition time from the NT-to-NO state is found to be a few seconds with high intensity of input and exciting beams because of the photoinduced anisotropic effect of azobenzene films. With lower intensity, the NT-to-NO transition time becomes relatively slow (tens of seconds). In the absence of an exciting beam, the films are not transparent as the polarization of input light is not rotated and blocked by the polarizer behind the sample. The response time of observed induced anisotropy is in agreement with earlier reports of the time evolution of photoinduced birefringence observed in side-chain polymers containing aminonitro azobenzene.<sup>26</sup> However, there are environments in which photoinduced reorientation is much faster. For example, in Langmuir-Blodgett films of side-chain polymers containing some derivatized aminoazobenzene chromophores, the anisotropy buildup time is less than 20 ns.<sup>27</sup> It is suggested that the primary driving mechanism for induced anisotropy in these films is not *trans-cis-trans* isomerization, but a vibronic dissipation of the electronic excitation energy that increases the rotational mobility of the chromophores collectively. Techniques are also available to enhance the birefringence, and hence the low-intensity transmission through the film if required. One way to do this



would be to shine red light on the sample to photoassist the *cis-trans* isomerization.<sup>28,29</sup> Birefringence can also be promoted by a controlled heating of the sample to certain optimal temperatures below the glass transition temperature.<sup>26</sup> Similarly, choosing a higher visible wavelength for the input beam should result in a corresponding higher photoinduced anisotropy, in addition to a lower absorption in the film. Apart from the protection of sensitive detectors, one practical application of this device would be a user-friendly laser goggle for protection against low-power cw lasers. According to the American National Standard for Safe Use of Lasers (ANSI Z136.1, 2000), a visible laser (400–700 nm) operating at less than a 1-mW power is considered safe for an exposure time of 0.25 s or less. Unfortunately, however, even some laser pointers can emit 5 mW of power that can be hazardous if viewed even for a short time. Therefore laser eye protection even at a low-power region is extremely important.

### 3. Conclusion

We have studied the optical power-limiting properties of an azobenzene material based on photoinduced anisotropic effects. The photoinduced anisotropy leads to an enhanced transmission of the input beam at low input intensities and output clamping at high input intensities. The limiting threshold is adjustable. Crossed polarizers ensure absolute safety of the detector in the event of any malfunction in the system. Because the limiting mechanism is general, the device can be operated at different wavelengths with suitable materials. In addition, the azobenzene materials are found to be stable when exposed to cw as well as pulsed lasers. In the future such media may be useful to limit high-energy fast laser pulses by our scheme.

This research is supported in part by a Broad Agency Announcement contract DAAD 16-01-C-0018 from the U.S. Army Natick Research Laboratory.

### References

1. T. Xia, D. J. Hagan, A. Dogariu, A. A. Said, and E. W. V. Stryland, "Optimization of optical limiting devices based on excited-state absorption," *Appl. Opt.* **36**, 4110–4122 (1997).
2. R. Lepkowitz, A. Kobayakov, D. J. Hagan, and E. W. V. Stryland, "Picosecond optical limiting in reverse saturable absorbers: a theoretical and experimental study," *J. Opt. Soc. Am. B* **19**, 94–101 (2002).
3. N. V. Kamanina and A. I. Plekhanov, "Mechanisms of optical limiting in fullerene-doped  $\pi$ -conjugated organic structure demonstrated with polyimide and COANP molecules," *Opt. Spectrosc.* **93**, 408–415 (2002).
4. M. V. Gryaznova, V. V. Danilov, M. A. Belyaeva, P. A. Shakhverdov, O. V. Chistyakova, and A. I. Khrebtov, "Optical limiters based on liquid-crystal microlenses," *Opt. Spectrosc.* **92**, 614–618 (2002).
5. G. Zhou, X. Wang, D. Wang, Z. Shao, and M. Jiang, "Upconversion fluorescence and optical power limiting effects based on the two- and three-photon absorption process of a new organic dye BPAS," *Appl. Opt.* **41**, 1120–1123 (2002).
6. I. M. Belousova, V. A. Grigor'ev, O. B. Danilov, A. G. Kalintsev, A. V. Kris'ko, N. G. Mironova, and M. S. Yur'ev, "Role of light-induced scattering in the optical limitation of laser radiation on the basis of fullerene-containing media," *Opt. Spectrosc.* **90**, 292–301 (2001).
7. G. S. Maciel, N. Rakov, and C. B. Araújo, "Enhanced optical limiting performance of a nonlinear absorber in a solution containing scattering nanoparticles," *Opt. Lett.* **27**, 740–742 (2002).
8. W. Ji, A. K. Kukawadia, Z. C. Feng, and S. H. Tang, "Self-defocusing of nanosecond laser pulses in ZnTe," *J. Appl. Phys.* **75**, 3340–3343 (1994).
9. J. J. Liu, P. P. Banerjee, and Q. W. Song, "Role of diffusive, photovoltaic, and thermal effects in beam fanning in LiNbO<sub>3</sub>," *J. Opt. Soc. Am. B* **11**, 1688–1693 (1994).
10. D. I. Kovsh, S. Yang, D. J. Hagan, and E. W. V. Stryland, "Nonlinear optical beam propagation for optical limiting," *Appl. Opt.* **38**, 5168–5180 (1999).
11. J. E. Ludman, J. R. Riccobono, N. O. Reinhard, I. V. Semenov, Y. L. Korzinin, S. M. Shahriar, H. J. Caulfield, J. M. Fournier, and P. Hemmer, "Very thick holographic nonspatial filtering of laser beams," *Opt. Eng.* **36**, 1700–1705 (1997).
12. O. V. Andreeva, I. M. Belousova, V. G. Bespalov, Y. N. Efimov, V. N. Sizov, A. S. Cherkasov, E. Yu. Yutanova, and A. L. Pyait, "Recording dynamic holograms in toluene solutions of fullerene C<sub>60</sub>," *J. Opt. Technol.* **69**, 170–174 (2002).
13. M. Scalora, J. P. Dowling, C. M. Bowden, and M. J. Bloemer, "Optical limiting and switching of ultrashort pulses in nonlinear photonic band gap materials," *Phys. Rev. Lett.* **73**, 1368–1371 (1994).
14. P. Tran, "Optical limiting and switching of short pulses by use of a nonlinear photonic bandgap structure with a defect," *J. Opt. Soc. Am. B* **14**, 2589–2595 (1997).
15. R. Frey and C. Flytzanis, "Optical limitation in resonant Faraday media," *Opt. Lett.* **25**, 838–840 (2000).
16. G. E. Dovgalenko, M. Klotz, G. J. Salamo, and G. L. Wood, "Optically induced birefringence in bacteriorhodopsin as an optical limiter," *Appl. Phys. Lett.* **68**, 287 (1996).
17. P. Wu, L. Wang, J. Xu, and B. Zou, "Transient biphotonic holographic grating in photoisomerization azo materials," *Phys. Rev. B* **57**, 3874–3880 (1998).
18. K. Meerholz, B. L. Volodin, Sandalphon, B. Kippelen, and N. Peyghambarian, "A photorefractive polymer with high optical gain and diffraction efficiency near 100%," *Nature (London)* **371**, 497–500 (1994).
19. T. Ikeda and O. Tsutsumi, "Optical switching and image storage by means of azobenzene liquid-crystal films," *Science* **268**, 1873–1875 (1995).
20. P. Wu, D. V. G. L. N. Rao, B. R. Kimball, M. Nakashima, and B. S. DeCristofano, "Transient optical modulation with a disperse-red-1-doped polymer film," *Appl. Opt.* **39**, 814–817 (2000).
21. S. B. Kippelen, N. Peyghambarian, S. R. Lyon, A. B. Padias, and H. K. Hall, Jr., "Dual-grating formation through photorefractivity and photoisomerization in azo-dye-doped polymers," *Opt. Lett.* **19**, 68–70 (1994).
22. R. A. Hill, S. Dreher, A. Knoesen, and D. R. Yankelevich, "Reversible optical storage utilizing pulsed, photoinduced, electric-field-assisted reorientation of azobenzenes," *Appl. Phys. Lett.* **66**, 2156–2158 (1995).
23. P. Chen, X. Wu, X. Sun, J. Lin, W. Ji, and K. L. Tan, "Electronic structure and optical limiting behavior of carbon nanotubes," *Phys. Rev. Lett.* **82**, 2548–2551 (1999).
24. For a recent review see C. Dekker, "Carbon nanotubes as molecular quantum wires," *Phys. Today* **52**, 22–28 (1999).
25. R. Philip, G. Ravindra Kumar, N. Sandhyarani, and T. Pradeep, "Picosecond optical nonlinearity in monolayer-protected gold, silver, and gold-silver alloy nanoclusters," *Phys. Rev. B* **62**, 13160–13166 (2000).
26. D. H. Choi, "Effect of temperature on photoinduced reorienta-

- tion of azobenzene chromophore in the side chain copolymers," Bull. Korean Chem. Soc. **20**, 1010–1016 (1999).
27. S. P. Palto, V. A. Khavrichiev, S. G. Yudin, L. M. Blinov, and A. A. Udalyev, "On a model of photo-induced optical anisotropy in Langmuir-Blodgett films: low temperature studies," Mol. Mater. **2**, 63–68 (1992).
  28. P. Wu, D. V. G. L. N. Rao, B. R. Kimball, M. Nakashima, and B. S. DeCristofano, "Nonvolatile grating in an azobenzene polymer with optimized molecular reorientation," Appl. Phys. Lett. **78**, 1189–1191 (2001).
  29. P. Wu, D. V. G. L. N. Rao, B. R. Kimball, M. Nakashima, and B. S. DeCristofano, "Enhancement of photoinduced anisotropy and all-optical switching in Bacteriorhodopsin films," Appl. Phys. Lett. **81**, 3888–3890 (2002).